Project: Cation Diffusion Rates in Selected Minerals *and* Atomistic Simulation of Minerals

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Objective: Determine experimental and theoretical cation diffusion coefficients for carbonate minerals for evaluating disequilibrium behavior in geological, nuclear waste, energy, and materials concerns.

Results: The electronic polarization of oxygen ions has been explicitly incorporated in a shell model to better simulate the structure of calcite and related rhombohedral carbonate minerals. Pair-potentials for Ca^{2+} ions and C and O comprising the carbonate molecular ion were simultaneously fitted to experimental lattice, elastic, dielectric, and vibrational data for calcite, and the structure and elastic properties of aragonite. The resulting potential parameters for the CO_3^{2-} group were then transferred to models for the structures and bulk moduli of the carbonate minerals incorporating Mn, Fe, Mg, Ni, Zn, Co, Cd, and thus a fully-consistent set of interaction parameters for calculating the properties of the carbonate minerals was obtained. Defect energies for doping the divalent cations into the calcite structure, and for calcium and carbonate ion vacancies were calculated. In addition, various disorder types for dolomite, including anti-site defects, stacking defects, and the energy related to increasing the Ca/Mg ratio in the dolomite structure were simulated. The theoretical
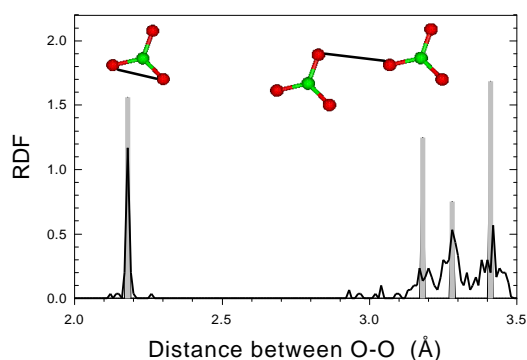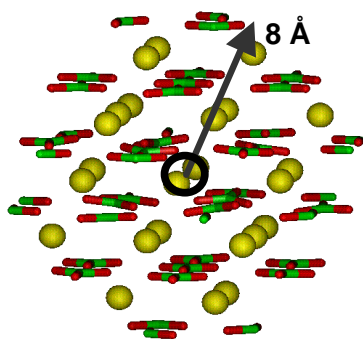
enthalpy for dolomite ordering (34.4 kJ/mol) compares very well with experimental measurements.

Figures: Distortion of CO_3^{2-} groups about Ca vacancy in calcite (left); Radial distribution function plot of variation of O-O distances due to vacancy (black line) relative to perfect crystal (gray line) (right).

Significance: This work provides the first general and consistent set of interaction potentials for the simulation of bulk and surface structures of calcite, aragonite, and other related metal carbonate phases. The theoretical treatment allows for the determination of the relative stability of various point defects in calcite, as related to the mechanisms of cation diffusion, and provides a basis for evaluating the energetics of dolomitization. These results also provide an atomistic foundation for examining the mechanisms of aqueous interactions with the various carbonate surfaces.

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